CAPSULES notes and applications from BASi

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July 1997

Electrochemical Impedance Spectroscopy
9. Investigation of Underpaint Corrosion

A variety of methods are available for protecting metals from corrosive environments, thereby minimizing corrosion. These typically include mechanical surface treatments (e.g., sand blasting, brushing) and/or chemical surface treatments (e.g., chromatation, phosphatation), followed by the application of organic films (paints) with various properties (e.g., primers, adhesion promoters and top coats). The effectiveness of such treatments depends critically on the presence of defects in the protective coatings, their resistance to water penetration, their adhesion and the reactivity of the interface. Hence, there is a need for a technique for investigating the corrosion of metal surfaces subjected to these treatments. In this Capsule, the use of Electrochemical Impedance Spectroscopy (EIS) for such investigations is examined.

Reference

Electrochemical Impedance Spectroscopy as a Tool for Investigating Underpaint Corrosion, P.L. Bonora, F. Deflorian and L. Fedrizzi, Electrochim. Acta 41 (1996) 1073-1082.

Method

Electrochemical impedance spectroscopy (EIS) is a powerful method for investigating processes occurring at the electrode/electrolyte interface. Since a range of frequencies is used, processes occurring at different rates (e.g., diffusion through a protecting layer and charge transfer at the electrode surface) can be detected within one experiment. In addition, EIS is a non-destructive method.

Results

A general equivalent circuit for modeling electrochemical processes at a metal surface covered with an organic films is shown in F1 (1). R_u represents the uncompensated solution resistance, C_c and R_p are the capacitance and resistance associated with the organic film and Z_f represents the electrochemical processes occurring at the metal surface. The nature of Z_f varies with both the metal substrate and the type of protective surface preparation used.

Perhaps the simplest form of Z_f is a parallel combination of the double-layer capacitance (C_{dl}) and the

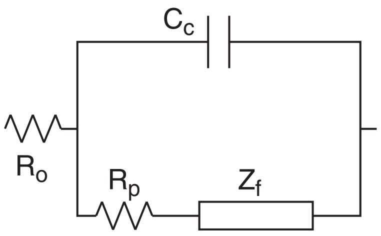

Figure 1. *General equivalent electrical circuit for metals coated with organic films.*

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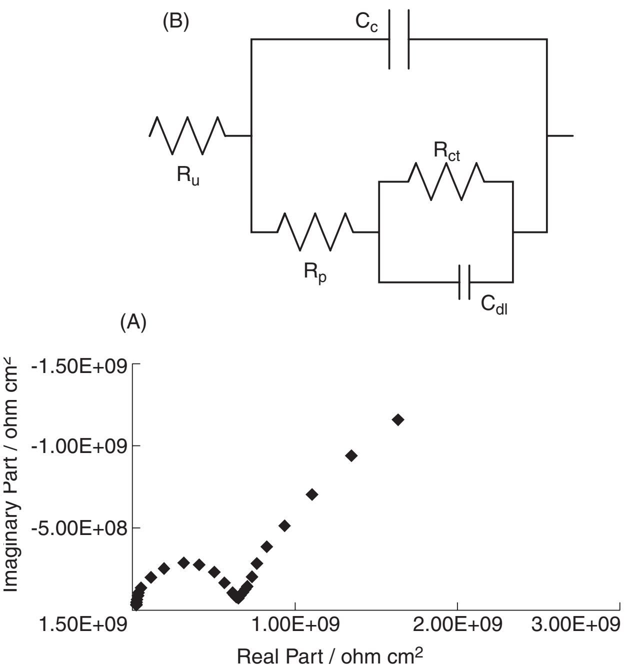

Figure 2. *(A) Nyquist plot for a sample of fluoropolymer-coated steel (30 μm) after immersion for 30 days in 0.3 % sodium sulfate solution. Figure adapted from the primary reference. (B) Equivalent circuit for impedance spectrum shown in F2A.*

charge transfer resistance (R_{ct}). This circuit is shown in F2B, and gives rise to the Nyquist plot shown in F2A, in which the time constants of the two processes are clearly resolved (this spectrum was recorded for a sample of sand-blasted mild steel coated with a 30 μm layer of a fluoropolymer after 30 days immersed in 0.3 % sodium sulfate solution). The semi-circle at high frequency was attributed to the organic coating.

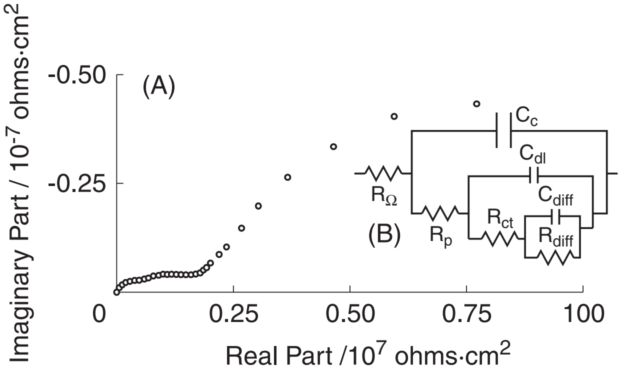

Figure 3. *(A) Nyquist plot for a sample of epoxy-coated galvanized steel with a macro-defect after immersion in 3.5 % sodium chloride solution. Figure adapted from the primary reference. (B) Equivalent circuit for impedance spectrum shown in F3A.*

A similar impedance spectrum was recorded for galvanized steel (i.e., steel covered with a layer of zinc metal) coated with an epoxy film after immersion in 3.5 % sodium chloride solution. However, the introduction of an artificial defect (about 0.1 mm^2) leads to the appearance of a third time constant (F3A), which was attributed to diffusion processes associated with the products of the corrosion reactions (the equivalent circuit is shown in F3B).

The presence of different time constants (due to different processes) is often more clearly resolved in the Bode plot. The Bode plot of a sample of epoxy-coated AISI 430 stainless steel with macro-defects after 3 days immersed in 3.5 % sodium chloride solution is shown in F4A. Three processes are clearly resolved in the phase angle vs. log frequency plot. In this case, the third process is associated with the capacitance (C_{ox}) and resistance (R_{ox}) associated with the oxide layer on the metal surface (the equivalent circuit is shown in F4B).

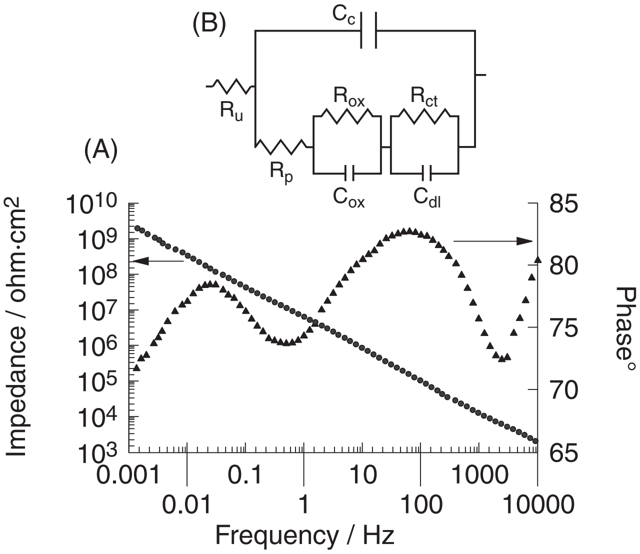

Figure 4. *(A) Bode plot for a sample of epoxy-coated AISI 430 stainless steel with macro-defects after 3 days immersed in 3.5 % sodium chloride solution. Figure adapted from the primary reference. (B) Equivalent circuit for impedance spectrum shown in F4A.*

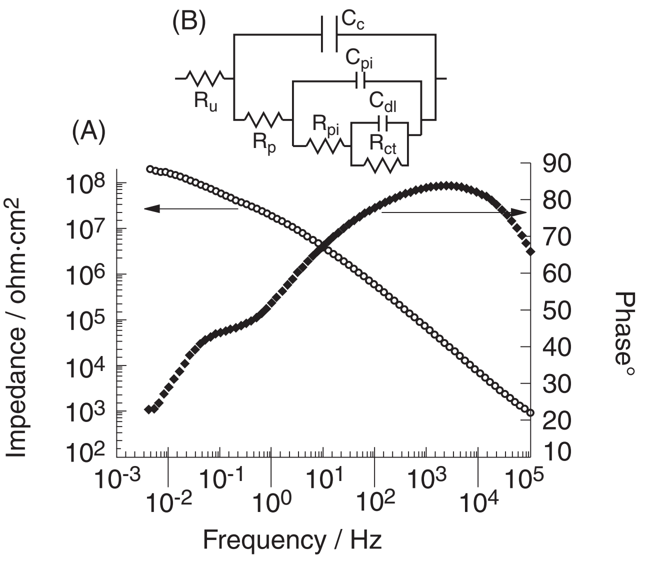

Figure 5. *(A) Bode plot for a sample of Al-Zn alloy coated with an epoxy primer containing strontium chromate pigments after immersion in 0.3 % sodium sulfate solution. Figure adapted from primary reference. (B) Equivalent circuit for impedance spectrum shown in F5A.*

The addition of pigments to the organic coating can also lead to the introduction of another time constant into the impedance spectrum. This is illustrated in F5A, which shows the Bode plot for a sample of Al-Zn alloy coated with an epoxy primer containing strontium chromate pigments after immersion in 0.3 % sodium sulfate solution. This spectrum was fitted using the equivalent circuit shown in F5B, in which the third time constant is attributed to the resistance (R_{pi}) and capacitance (C_{pi}) associated with the pigments. It should be noted that the values of these RC parameters, as well of those associated with the organic film, did not vary as the applied DC potential was changed. In contrast, the values of the parameters associated with the interfacial processes (C_{dl} and R_{ct}) did show a large potential dependence, as would be expected.

Once the physical parameters of the system have been identified through the selection of the appropriate equivalent circuit, the values of these parameters and their variation with changing conditions can be used to characterize the effectiveness of the various surface treatments. For example, the absorption of water by an organic film (which typically leads to loss of film adhesion) can be monitored by examining the variation in the film capacitance C_c. The decrease in the film resistance R_p is associated with the total defect area within the film. Rct is a direct measure of the rate of the corrosion reaction occurring at the metal surface. Changes in C_{dl} can be indicative of delamination.

References

1. *F. Mansfeld, M. Kendig and S. Tsai, Corrosion 38 (1983) 478-485.*